



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09K 11/06, H01B 1/12, C08G 61/10, H05B 33/14		A1	(11) International Publication Number: WO 99/20711
			(43) International Publication Date: 29 April 1999 (29.04.99)
(21) International Application Number: PCT/GB98/03154		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 21 October 1998 (21.10.98)			
(30) Priority Data: 9722102.2 21 October 1997 (21.10.97) GB 9814815.8 8 July 1998 (08.07.98) GB			
(71) Applicant (for all designated States except US): CAMBRIDGE DISPLAY TECHNOLOGY LTD. [GB/GB]; 181a Huntingdon Road, Cambridge CB3 0DJ (GB).		Published <i>With international search report.</i>	
(72) Inventors; and (75) Inventors/Applicants (for US only): HOLMES, Andrew, Bruce [AU/GB]; 19 Newton Road, Cambridge CB2 2AL (GB). CHUAH, Beng, Sim [MY/GB]; Queen's College, Silver Street, Cambridge CB3 9ET (GB). CACIALLI, Franco [IT/GB]; 52 Brampton Road, Cambridge CB1 3HL (GB). MORATTI, Steven, Carl [NZ/GB]; 28 Awlstone Road, Cambridge CB3 9JH (GB).			
(74) Agents: DANIELS, Jeffrey, Nicholas et al.; Page White & Farrer, 54 Doughty Street, London WC1N 2LS (GB).			
(54) Title: POLYMERIC MATERIALS FOR ELECTROLUMINESCENT DEVICES			
(57) Abstract Provided is a conjugated poly(1,4-arylene vinylene) compound comprising an arylene unit having adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

POLYMERIC MATERIALS FOR ELECTROLUMINESCENT DEVICES

The present invention is directed to polymers for use in electric, electronic, optical and optoelectronic devices, e.g. polymer-based light-emitting devices, such as light emitting diodes (LEDs). In particular, the present invention concerns poly(1,4-arylene vinylene)s which have improved photoluminescence and/or electroluminescence efficiencies.

The potentially high photoluminescent quantum yield in organic semiconductors has made light emission through charge injection under an applied field (electroluminescence) a reality. This has thus resulted in the use of organic materials for LEDs, with the use of polymers having an advantage over smaller organic compounds in improving structural stability and processibility of the organic layers.

The first polymer-based LEDs consisted of an emissive layer of poly(1,4-phenylene vinylene) (PPV) sandwiched between indium tin oxide (ITO) as the hole injection electrode and aluminium or calcium as the electron-injecting electrode (Burroughes et al., *Nature*, 1990, 347, 539). This has been followed in other polymers for LED applications, with emphasis on the tuning of the emission colour by controlling the substitution pattern and the effective conjugation length in the polymer.

The route used for the synthesis of PPVs for LEDs has been predominantly the Wessling sulphonium salt precursor route (U.S. Pat. 3,401,152/1968 Wessling *et al.*) while another important method of Gilch (Gilch *et al.*, *J. Poly. Sci.* 1-A, 1966, 4, 1337), involved dehydrohalogenation of bis(halomethyl) benzene monomers with excess potassium *t*-butoxide to directly obtain the conjugated polymer. This protocol has been applied to the red emissive poly(2,5-dialkoxy-1,4-phenylene vinylene)s which have a typical absolute PL efficiency of ca. 15-20%. Most commonly the preparation has referred to poly[2-methoxy-5(2'-ethylhexyloxy)-1,4-phenylene vinylene] (Wudl, U.S. Pat. 5,189,136/1990). A modification of this route by Swatos and Gordon, based on the chloro-precursor route, used one equivalent of base to form the chloro-substituted soluble precursor polymer, which was then thermally converted to form the fully conjugated polymer [Swatos and Gordon, *Polym. Prepr.*, 1990, 31 (1), 505]. This route has since

been used by various groups to make alkyl-, aryl- and alkoxy-substituted PPVs (Hsieh *et al.*, *Adv. Mater.*, 1995, 7, 36; *Polym. Adv. Tech.*, 1997, 8, 392; U.S. pat. 5,558,904; Sarnecki *et al.*, *Synth. Met.*, 1995, 69, 545).

There is still a need to provide photoluminescent and electroluminescent polymers, which are easily manufactured and are processible. There is also still a need for polymers having improved photoluminescence and electroluminescence efficiencies.

It is an object of the present invention to solve the above problems. Accordingly, the present invention provides a conjugated poly(1,4-arylene vinylene) compound comprising an arylene unit having adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.

The present invention also provides use of a poly(arylene vinylene) compound comprising an arylene unit having adjacent substituents, in an electric, electronic, optical or optoelectronic component or device for producing blue-shifted electroluminescence or photoluminescence in said device.

The substituents may affect the electronic structure of the compound by exerting a steric or stereoelectronic effect, such as a twisting of the polymer backbone to accommodate their steric bulk, which twisting leads to a reduction in the conjugation of the compound. The reduction in conjugation in turn leads to a blue-shift in luminescence. Additionally, the substituents may possess one or more lone pairs of electrons which may interfere with the conjugation in the polymer to cause the blue-shift in luminescence.

The blue-shift is a blue-shift as compared with a hypothetical compound, this being the same polymer in which the orientation of the substituents (whether resulting from their steric bulk or some electronic effect) has no effect on the electronic structure of the compound. Thus, for example, the blue-shift may be a blue-shift resulting from a reduction in conjugation caused by

twisting the backbone of the polymer to the degree required to accommodate the steric bulk of the substituents.

The present invention describes the surprising discovery of efficient blue-shifted emission from poly-1,4-(arylene vinylene)s having adjacent substituents, preferably 2,3-disubstituted PPV-based materials and their use in LEDs. This invention explores unconventional substitution patterns, e.g. in the case of poly(phenylene vinylenes) (PPVs) at the 2,3-positions on the phenyl ring as opposed to the standard 2,5-disubstituted PPVs and thus provides a means of tuning the colour of emission. In addition, the present invention provides a luminescent polymer that is both soluble and directly obtainable, preferably by the Gilch route. The invention refers to the synthesis of improved materials and their application in organic LEDs.

The present invention also provides materials-based light-emitting devices, such as light emitting diodes (LEDs), in which the use of a layer of emissive polymer enables efficient devices to be constructed using aluminium or calcium cathodes. The polymer is a poly(1,4-arylene vinylene) having adjacent aryl substituents, preferably a poly(1,4-phenylene vinylene) (PPV) derivative, having substituents on the 2,3-positions of the phenylene ring. This substitution pattern produces a blue-shifted emission and high PL and EL device efficiencies. The polymerisation route is simple, the polymer is soluble, and displays good film forming properties with high photoluminescence in the solid state.

The invention will now be described in further detail by way of example only, with reference to the accompanying drawings, in which:

Figure 1 shows the X-ray crystal structure of oligomer 9;

Figure 2 shows absorption and PL spectra of films of oligomer 9;

Figure 3 shows absorption spectra of PDB PPV 1 compared with a PPV film;

Figure 4 shows PL spectra of PDB-PPV 1 compared with PPV film and EL spectra of a bilayer device (configuration ITO/PPV/PDB-PPV 1/Ca)

Figure 5 shows a plot of current density vs. applied voltage for a bilayer device (configuration ITO/PPV/PDB-PPV/Ca)

Figure 6 shows absorption and photoluminescence spectra of films of copolymers 12 and 13;

Figure 7 shows I-V-L plots for single layer device ITO/15C5-DB PPV 12/Al;

Figure 8 shows I-V-L plots for single layer device ITO/15C5-DMOS PPV 13/Al;

Figure 9 shows I-V-L plots for double layer device ITO/PPV/15C5-DMOS PPV 13/Al, at drive voltages *ca.* 14V, EL quantum efficiency up to 2.0%;

Figure 10 shows a CV plot of 15C5-DB PPV copolymer 12;and

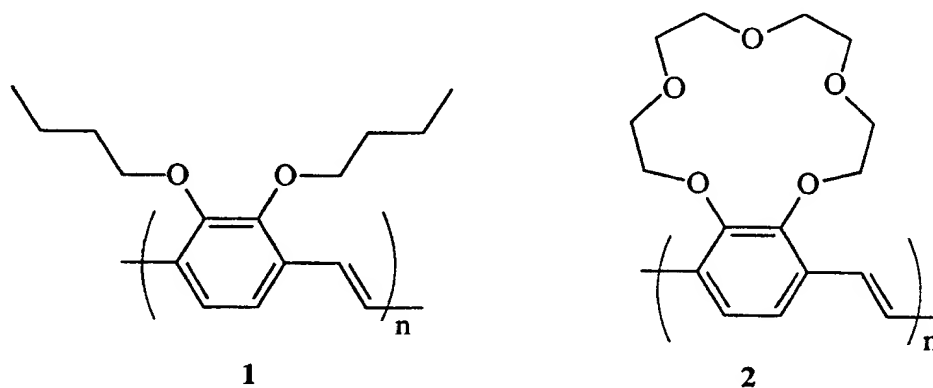
Figure 11 shows a CV plot of 15C5-DMOS PPV copolymer 13.

The electroluminescent (EL) devices according to the present invention are injection-type diodes in which at least one active layer (EL layer) and one or more charge transport layers (if desired) are sandwiched between two different conducting layers (electrodes). One electrode is a hole-injecting translucent or transparent electrode while the other is an electron-injecting electrode. The electrodes are electrically connected to each other and to a source of current to create a complete circuit. Improved efficiencies may be obtained using bilayer devices with PPV or hole transporting layers e.g. poly(vinyl carbazole) (PVK).

This invention refers in one specific embodiment to the polymer, poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] 1 which can be prepared using the dehydrohalogenation method with base (potassium tert-butoxide). The resultant polymer has high molecular weight and its alkyl chains enable solubility in organic solvents such as chloroform and tetrachloroethane. Surprisingly, the solid film fluoresces with high efficiency (absolute PL efficiency 40%) in the

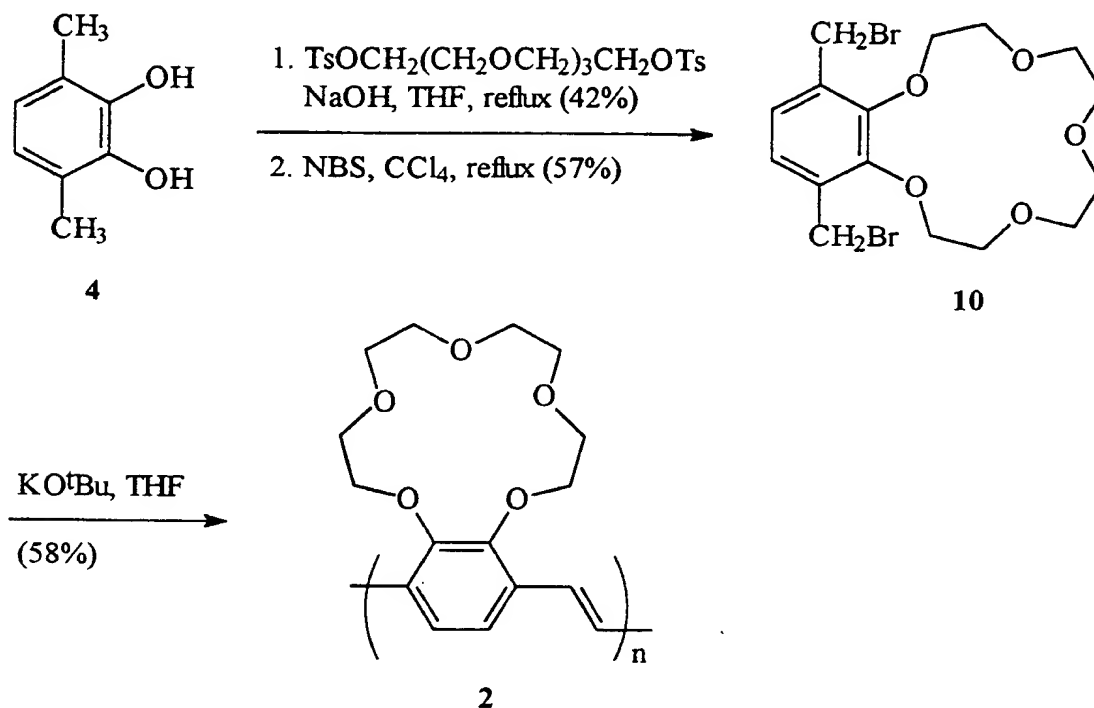
yellow green region despite having alkoxy substituents. The present invention also concerns a further embodiment relating to the polymer 2. In addition to its emissive properties in PL and EL devices it has the potential to serve as a component of a sensor owing to its affinity for metal ions.

In a further embodiment, the invention extends to the fluorescent oligomer 9 which has been synthesised using the Wadsworth-Emmons reaction of a dialkoxybenzyl bisphosphonate 8 and dialkoxy-benzaldehyde 7. Evidence for the origin of the blue-shifted emission and possible high fluorescence efficiency comes from the single crystal X-ray study of 9 which shows that the aromatic rings are twisted in a notable manner, thus resulting in the disruption of the effective conjugation length of the polymer backbone. The localisation of the conjugation could also be due to the cisoid-like disposition of the styryl substituents in 9 (see Figure 1).



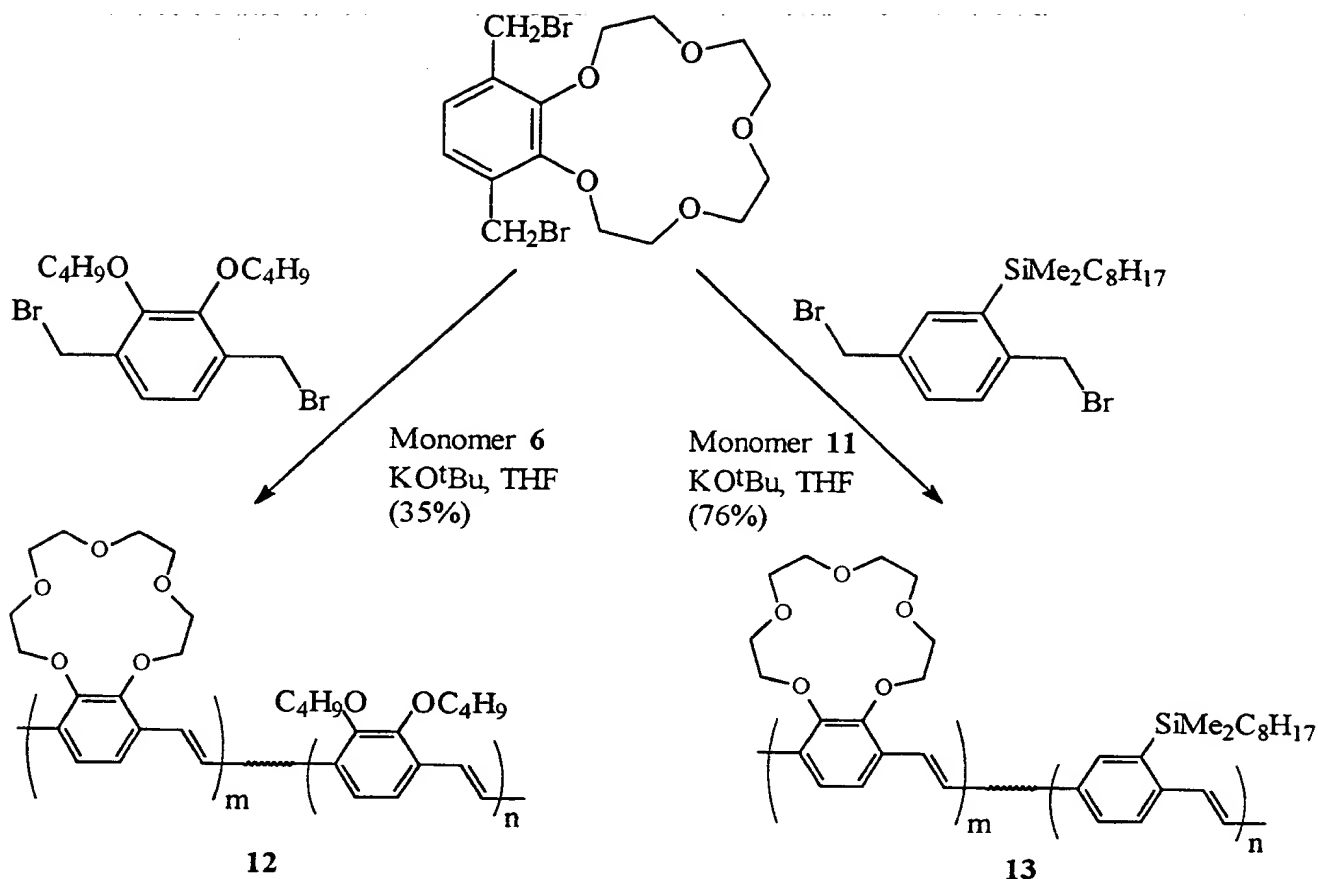
Scheme 1: Structure of the poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] (PDB-PPV) 1 and the crown ether analogue 2

The crown ether analogue **2** is also fluorescent. It can be prepared as shown in Scheme 2 below:



Scheme 2: Preparation of 15C5 crown ether **2**

As the polymer **2** is also luminescent it can be used advantageously in light emitting electrochemical devices and other devices where chelation of various metal ions, preferably lithium, can lead to ionically doped materials fabricated out of a homogeneous phase rather than from a blend of more than one polymer which may phase-separate. Such doping can lead to reduced barriers for charge injection into the emissive layers. Statistical copolymers derived from dehydrohalogenation condensation polymerisation of the building block **10** with either the DMOS precursor **11** or the dibutoxy precursor **6** afford efficient devices (Scheme 3). The ratio of m:n may range from 10:1 to 1:10, preferably ca. 1:1.



Scheme 3: Statistical copolymers 12 and 13

Two layer devices were fabricated using 1 as follows. A layer of a PPV precursor polymer, fabricated according to a sulphonium precursor route ["Precursor route chemistry and electronic properties of poly(p-phenylene vinylene), poly(2,5-dimethyl-p-phenylene vinylene) and poly(2,5-dimethoxy-p-phenylene vinylene)" P. L. Burn, D. D. C. Bradley, R. H. Friend, D. A. Halliday, A. B. Holmes, R. W. Jackson and A. Kraft, *J. Chem. Soc. Perkin Trans. 1*, 1992, 3225-3231], was spin-coated onto a glass plate coated with ITO and thermally converted to PPV. In the other type of bilayer device, a transporting layer of PVK was spin-coated from solution directly onto ITO.

Next, a layer of the polymer poly[(2,3-dibutoxy)-1,4-poly(phenylene vinylene)] (PDB-PPV) 1 was spin-coated onto the PPV layer followed by a layer of aluminium or calcium deposited under

vacuum onto the polymer layer. Contacts were attached and a connection made to a DC power source. Application of a forward bias voltage resulted in emission of yellow-green light with an emission maximum at about 2.3 eV (*ca.* 550 nm), and a brightness in excess of 4,500 cd/m². Internal efficiencies of about 1.5% were observed with calcium as the cathode.

Based on the illustrative examples it is evident that highly efficient devices can be obtained by the dehydrohalogenation route to prepare adjacently substituted arylene vinylene polymers, such as 2,3-disubstituted-1,4-phenylene vinylene polymers from monomers carrying aryl, heteroaryl, alkyl, and branched alkyl substituents linked either by carbon or heteroatom linkages to the aromatic backbone of the polymer.

The adjacent substituents can be selected from H, R, RO-, RS-, and RR'N-, where R=C₅H₁₁, C₆H₁₃, C₇H₁₅ or C₈H₁₇, etc. and branched derivatives thereof, and aryl (Ar) where Ar = aryl or heteroaryl or fused derivatives thereof. Preferable substituents are those which solubilise the final polymer. These include branched alkyl, aralkyl and the corresponding alkoxy derivatives. The most preferred substituent is the butyloxy, and other preferred substituents are ethylhexyl(oxy) and 3',7'-dimethyloctyl (oxy). Other carbon chains such as alkyl or alkoxy substituents carrying up to ten carbon atoms and branching substituents are advantageous. Such substituents could be selected in any combination, and are not limited to those listed.

Similar effects can be achieved with any conjugated polyarylenevinylene polymer or other conjugated polymer (polyfluorene, polythienylene, polynaphthalene, polyphenylene, polypyridine, polyquinoline, polyquinoxaline, poly[thienylene-co-phenylene] etc.) or a copolymer arising from a fluorescent unit carrying a distyrylbenzene fragment with the 2,3-disubstitution at least on the aromatic rings. The preferred polymers arise from poly(arylene vinylene) conjugated units carrying an adjacent disubstitution pattern. Most preferably, 2,3-disubstituted bishalomethylbenzene derivatives serve as starting monomers for the conjugate polymer products.

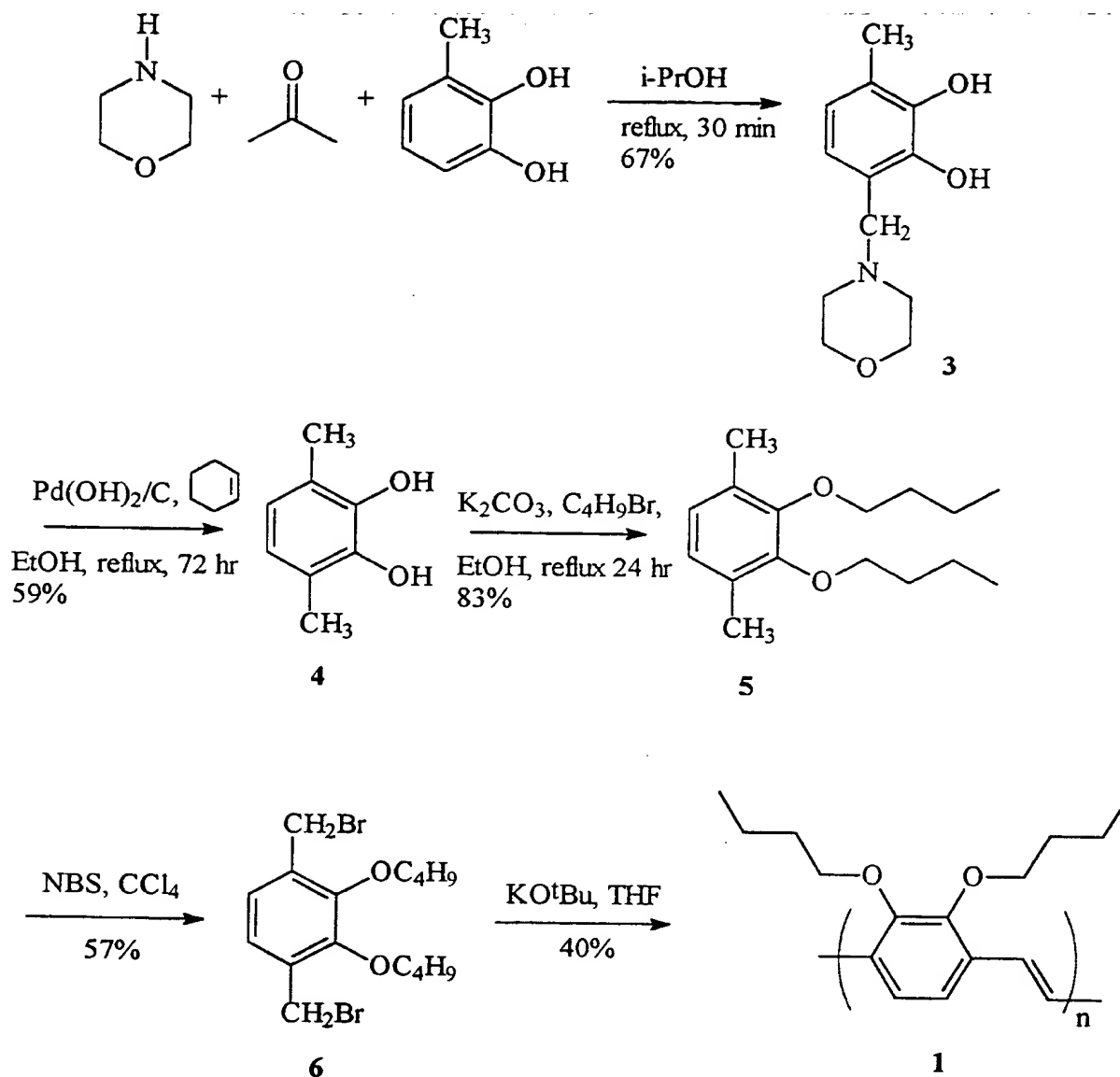
The preferred synthesis involves dehydrohalogenation condensation polymerisation using potassium t-butoxide as a base in various solvents such as tetrahydrofuran or dioxane. The resulting polymer is solution processible and has a good film forming property for polymer

electroluminescent devices. Polymers for 1,4-bis(halomethylbenzene) monomers have been disclosed in US 5,558,904. These afforded insoluble polymers. The adjacent disubstitution in the present invention is achieved owing to the method of synthesis of the polymer, and leads to a product polymer that is solution processible, and having a surprising fluorescence emission wavelength and efficiency.

Previous examples with a 2,3-diphenyl (diaryl) substitution pattern as disclosed in US 5,558,904 would not be expected to demonstrate these features, based on the lack of solubility of the final polymer. This is disclosed in detail in H. Antoniadis *et al.*, *Polym. Adv. Tech.*, 1997, **8**, 392. In that case solution processibility required the use of a precursor route to allow processing and generation of the final polymer.

Examples

A method of preparing the conjugated polymer PDB-PPV **1** involves the preparation of the monomer of formula $\text{Br-CH}_2\text{-Ar-CH}_2\text{-Br}$ which is subjected to polymerisation with six equivalents of base (potassium tert-butoxide preferably in THF or dioxane) to give the desired polymer, which is soluble in organic solvents such as chloroform and tetrachloroethane. The synthesis of the polymer is shown in scheme 4 below:



Scheme 4: Preparation of PBD PPV 1

Example 1: Preparation of monomer 6

Methyl catechol derivative **3** was synthesised by performing a Mannich reaction with formaldehyde and morpholine following the method described by Helgeson *et al.* (*J. Am. Chem. Soc.*, 1997, **99**, 6411). Transfer hydrogenation using palladium hydroxide on carbon to remove the morpholine group in the presence of a hydrogen donor (Hanessian *et al.*, *Synthesis*, 1981, **118**, 396) subsequently produced the dimethyl catechol **4** in reasonable yield (59%). *O*-alkylation was

then carried out using a copious excess of potassium carbonate and dibutyl bromide to give a reasonably high yield (83%) of dialkoxy-xylene 5. Radical bromination of the xylene with a slight excess of *N*-bromosuccinimide in carbon tetrachloride as given in Gruter *et al*, *J. Org. Chem.*, 59, 4473 gave the monomer 6 in comparatively high yield (57%).

Example 2: Preparation of polymer 1

A degassed solution of the monomer 6 (0.24 g, 0.6mmol) in dry THF (16 cm³) was added slowly over 20 min to a degassed solution of potassium tert-butoxide (0.41 g, 3.6 mmol) in dry THF (16 cm³) at room temperature. The reaction mixture was stirred at room temperature under nitrogen for 18 h, after which it was poured into methanol. The resultant yellow precipitate was collected by filtration and re-precipitated into methanol. The polymer 1 was collected as a bright yellow solid (60 mg, 40%).

Found: C, 76.6; H, 9.1; Br, 0; [C₁₆H₂₂O₂]_n requires C, 78.0; H, 9.0; Br, 0 %

GPC assay in CHCl₃ revealed *M_w* 2,120,000, *M_n* 361,000 and *M_w/M_n* 5.9;

λ_{max} (CHCl₃)/nm 444; λ_{max} (film)/nm 450;

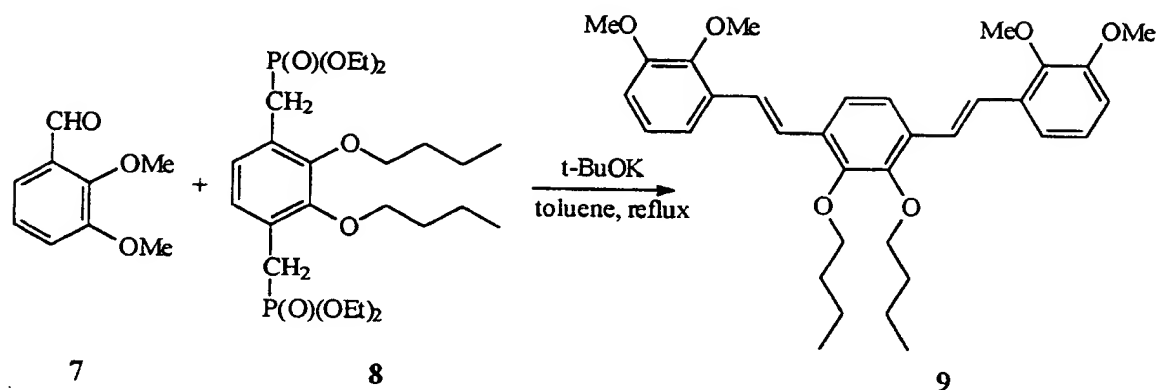
PL emission (max)/nm 551 (2.25 eV); PL efficiency 40 %; EL emission (max)/eV 2.28.

Example 3: Fabrication of a 2-layer LED with polymer 1

A film of PPV (ca. 100 nm in thickness) was prepared by spin-coating a solution of a sulphonium precursor polymer onto a glass plate coated with indium tin oxide and thermally converting the film at 230°C in vacuum for 6h. A 1% (w/v) solution of the polymer 1 in chloroform was spin-coated on top of the converted PPV film to give a uniform film of about 100 nm thick. The structures were placed on top of a mask, permitting the deposition of aluminium or calcium on the coated film surface inside a metal evaporator. Metal layers were of typically 500-1000 Å in thickness. Metal contacts were then attached to the electrodes and connected to a DC source. The active device area was typically 4 mm².

The bilayer device (ITO/PPV/PDB-PPV/Ca) shows maximum efficiency 1.5 % with luminance in excess of 4,500 cd/m² with turn-on voltage at 9V. A bilayer device was also constructed with PVK as the hole-transporting layer produced a maximum efficiency of 0.6% with Al cathodes.

Example 4: Preparation of the model oligomer 9



Scheme 5: Preparation of dialkoxy-substituted oligomer 9

9 is obtained as pale green crystals, m.p. 80-81; λ_{max} (CHCl₃) 362 nm, (film) 366 nm; blue-green fluorescence, PL_{max} (film) 2.6 eV

A mixture of the 2,3-dimethoxybenzaldehyde 7 (0.33 g, 2.0 mmol) and 1,4-[(2,3-dibutoxy)xylylene]-bis(diethylphosphonate) 8 (0.52 g, 1.0 mmol) in toluene (10 cm³) was stirred and heated to ca. 100°C under an atmosphere of nitrogen. Potassium tert-butoxide (0.35 g, 3.0 mmol) was added all at once into the hot mixture resulting in a colour change to orange-brown. The mixture was then heated to reflux for 4 h. After allowing to cool to room temperature, toluene was added (20 cm³) followed by hydrolysis with acetic acid (10% aq., 20 cm³). The organic layer was separated, washed with water until the organic layer tested neutral. The organic fraction was the dried, followed by removal of the solvent under reduced pressure to yield a yellow oil. The product 9 was isolated by column chromatography (9:1 hexane:diethyl ether v/v) and further purified by recrystallisation from methanol to give greenish-white needles (0.35 g, 64%).

M.p. 80.0-81.0°C;

δ_{H} (250 MHz; CDCl₃) 7.49-7.47 (6H, m, Ar-H & CH=CH), 7.30-7.26 (2H, m, ArH_a), 7.08 (2H, t, *J* 8.0, ArH_b), 6.86-6.83 (2H, m, ArH_c), 4.04 (4H, t, *J* 6.6, ArOCH₂), 3.89-3.87 (12H, m, ArOCH₃), 1.88-1.77 (4H, m, CH₂), 1.64-1.49 (4H, m, CH₂), 1.00 (6H, t, *J* 7.2, CH₃);

δ_c (63.5 MHz; $CDCl_3$) 153.1 (C, Ar), 150.6 (C, Ar), 147.1 (C, Ar), 132.0 (C, Ar), 131.7 (C, Ar), 124.2 (CH, Ar), 124.1 (CH, Ar), 123.4 (CH, Ar), 121.0 (CH, Ar), 117.9 (CH, Ar), 111.3 (CH, Ar), 73.7 (OCH_2), 61.1 (OCH_2), 55.8 (OCH_2), 32.4 (CH_2), 19.4 (CH_2), 14.0 (CH_3);

m/z (CI) 547 (MH^+ , 75%), 402 (10), 166 (40), 72 (C_4H_8O , 60), 52 (C_4H_4 , 70);

Found (MH^+) 547.3060; $C_{34}H_{42}O_6$ requires 546.2981;

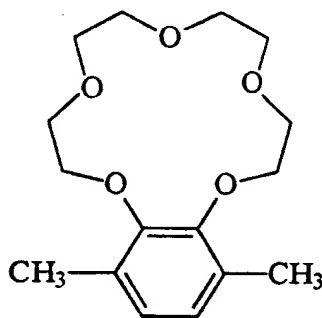
Found: C, 74.7; H, 7.8; $C_{34}H_{42}O_6$ requires C, 74.7; H, 7.8 %;

λ_{max} ($CHCl_3/nm$) 366; λ_{max} (film/nm) 362;

PL_{max} (film/nm) 477; PL efficiency (solid state) *ca.* 80%.

The X-ray structure of the oligomer 9 (see Figure 1) shows an unusual cisoid-like conformation around the *trans*-vinylene bond. The benzene rings are twisted out of the plane of the vinylene linkage by about 15° and the benzene rings in turn are twisted at a 30° angle from one another in a regular pattern. This twist will eventually cause an interruption in the polymer backbone conjugation after every 4 benzene rings. The oligomer shows high PL efficiency (*ca.* $8 \pm 8\%$) in the solid state.

Synthesis of Monomers

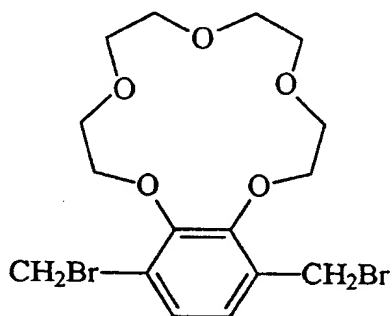


14

3,6-Dimethylbenzo-15-crown-5, 14

To a solution of dimethyl catechol 4 (2.5 g, 18 mmol) in tetrahydrofuran (110 cm^3) under a nitrogen atmosphere was added sodium hydroxide (1.44 g, 36 mmol). The mixture was left stirring for a hour, and a solution of tetraethyleneglycol-di-*p*-tosylate (9.05 g, 18 mmol) in tetrahydrofuran (50 cm^3) was added in dropwise over 30 min. The mixture was refluxed for 22 h. The mixture was cooled, the solvent removed and the residue taken up in dichloromethane

(200 cm³). The organic layer was extracted with water (3 x 100 cm³) and dried over MgSO₄. The solvent was removed under reduced pressure to yield a brown crude. The benzo crown ether was isolated by flash column chromatography (hexane followed by 9:1 hexane:ethyl acetate v/v) to yield the ether **14** as a colourless oil (2.2 g, 41%). *R*_f 0.25 (6:4 hexane:ethyl acetate v/v); ν_{\max} (KBr)/cm⁻¹ 2860, 1580, (Ar), 1281, 1134, 1081 (C-O); δ_{H} (400 MHz; CDCl₃) 6.79 (2H, s, Ar-*H*), 4.11 (2 x 2H, t, *J* 5.2, Ar-OCH₂), 3.96 (2 x 2H, t, *J* 5.2, ArO-CH₂CH₂), 3.74 (4 x 2H, m, OCH₂), 2.22 (6H, s, ArCH₃); δ_{C} (400 MHz; CDCl₃) 150.6 (C, Ar), 150.6 (C, Ar), 129.8 (C, Ar), 129.8 (C, Ar), 125.4 (CH, Ar), 125.4 (CH, Ar), 71.9 (CH₂), 71.9 (CH₂), 71.1 (CH₂), 71.1 (CH₂), 70.6 (CH₂), 70.6 (CH₂), 70.3 (CH₂), 70.3 (CH₂), 15.8 (CH₃), 15.8 (CH₃); *m/z* (CI) 297 (MH⁺, 20%), 244 (5), 164 (10); Found (MH⁺) 297.1702; C₁₆H₂₄O₅ requires 296, 1624; Found: C, 64.4; H, 8.1; C₁₆H₂₄O₅ requires C, 64.8; H, 8.2 %

**10**

3,6-Bis (bromomethyl)-benzo-15-crown-5, 10

A mixture of the benzo-crown ether **14** (1.77 g, 5.97 mmol), *N*-bromosuccinimide (2.18g, 12.2 mmol) and benzol peroxide (0.14 g, 0.6 mmol) in carbon tetrachloride (50 cm³) was heated to reflux for 5 h after which the succinimide had floated to the surface of the solvent mixture. After allowing to cool to room temperature, the mixture was filtered through Celite® and washed with ether. The filtrate was collected and the solvent removed under reduced pressure. The residue was taken up in ether (100 cm³) and the organic layer extracted with water (2 x 50 cm³). The organic fraction was dried over MgSO₄ and the solvent removed under reduced pressure to

produce the crude product as an orange-coloured solid. Recrystallisation from boiling hexane yielded the bis bromomethyl product **10** as a colourless solid **10** (0.56 g, 21 %). M.p. 127.5-128.5°C; R_f 0.32 (6:4 hexane:ethyl acetate v/v);

ν_{\max} (neat)/cm⁻¹ 2875, 1451 (Ar), 1287, 1146, 1057 (C-O), 677 (C-Br);

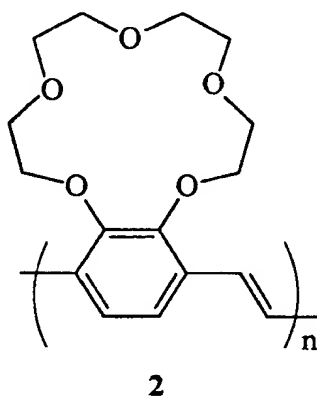
δ_H , (250 MHz; CDCl₃) 7.09 (2H, s, Ar-H), 4.53 (4H, s, CH₂Br), 4.33 (4H, t, J 5.0, ArOCH₂), 4.00 (4H, t, J 5.0, ArOCH₂CH₂), 3.75 (8H, m, OCH₂);

δ_C (100 MHz; CDCl₃) 150.9 (C, Ar), 150.9 (C, Ar), 133.4 (C, Ar), 133.4 (C, Ar), 126.1 (CH, Ar), 126.1 (CH, Ar), 72.6 (CH₂), 72.6 (CH₂), 71.1 (CH₂), 71.1 (CH₂), 70.4 (CH₂), 70.4 (CH₂), 27.7 (CH₂), 27.7 (CH₂);

m/z (CI) 470 (M+NH₄⁺, 58 %), 390 (5), 312 (12), 44 (15);

Found (M+NH₄⁺) 470.0178; C₁₆H₂₂O₅Br₂ requires 451.9835;

Found: C, 42.5; H, 4.8; Br, 35.2; C₁₆H₂₂O₅Br₂ requires C, 42.5; H, 4.9, Br 34.9 %



15C5-PPV, 2

A degassed solution of KO^tBu (0.1 g, 0.88 mmol) in dry THF (16 cm³) was added slowly over 20 min to a degassed solution of the dibromide monomer **10** (0.2 g, 0.44 mmol) in dry THF (16 cm³) at room temperature. The reaction mixture was stirred at ambient temperature under nitrogen for 18 h, after which it was poured into methanol (600 cm³) with stirring. The resultant yellow precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was re-dissolved in minimum CHCl₃ and re-precipitated into methanol (600 cm³). The solid was collected through filtration and dried *in vacuo* to afford the polymer **9** as an orange solid (75 mg, 58 %).

ν_{\max} (film)/ cm^{-1} 2925, 2867, 1492 (Ar), 1285, 1133 (C-O), 938 (trans-vinylene);

δ_{H} (400 MHz; CDCl_3) 7.50-7.25 (2H, br m, conjugated unit), 4.25 (4H, br m, ArOCH_2), 4.05 (4H, br m, $\text{ArOCH}_2\text{CH}_2$) 3.80 (8H, br m, OCH_2);

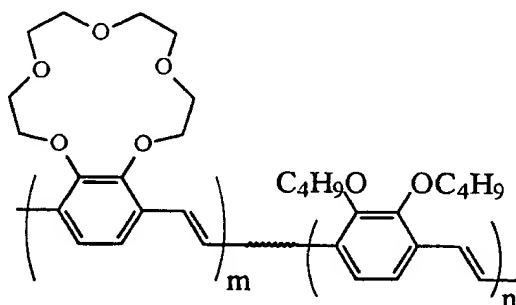
δ_{C} (100 MHz; CDCl_3) 150.5, 131.5, 121.0 (C, conjugated aromatic carbons), 71.5, 70.5, 70.5 (crown ether CH_2) (conjugated units not visible using 8,000 scans);

Found: C, 62.6; H, 6.8; Br, 1.4; $[\text{C}_{16}\text{H}_{20}\text{O}_5]_n$ requires C, 65.7; H, 6.9; Br, 0 %.

GPC assay in CHCl_3 revealed M_w 10.7×10^6 , M_n 126×10^3 and M_w/M_n 84;

λ_{\max} (film)/nm 442.

Synthesis of Copolymers



12

15C5-DB PPV copolymer, 12

A degassed solution of KO^tBu (0.26 g, 2.2 mmol) in dry THF (40 cm^3) was added slowly over 20 min to a degassed solution of a mixture of monomers, bis(bromomethyl)-benzo-15-crown-5 monomer 10 (0.2 g, 0.44 mmol) and 2,3-dibutoxy-1,4-bis(bromomethyl) benzene 6 (0.18 g, 0.44 mmol) in dry THF (40 cm^3) at room temperature. The reaction mixture was left stirring at ambient temperature under nitrogen for 6 h, and poured into methanol (500 cm^3) with stirring. The resultant orange precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was re-dissolved in minimum CHCl_3 and re-precipitated into methanol (500 cm^3). The solid was collected through filtration and dried *in vacuo* to afford the polymer as a bright orange solid (0.15 g, 35 %).

ν_{\max} (film)/ cm^{-1} 2956, 2869, 1436 (Ar), 1283, 1135 (C-O), 974 (trans-vinylene);

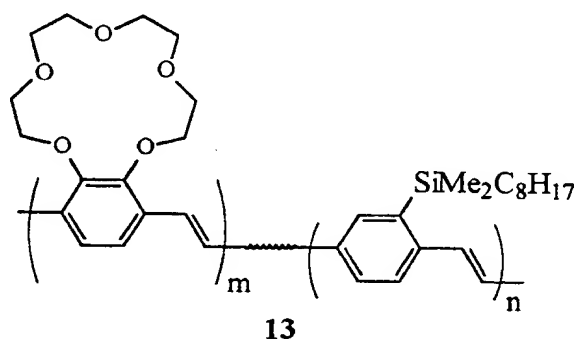
δ_H (400MHz; $CDCl_3$) 7.49-7.45 (H-conjugated units), 4.22-3.73 (2OH, m, br, OCH_2 & $ArOCH_2$), 1.84-1.57 (8H, m, br, CH_2), 1.03-0.99 (6H, m, br, CH_3);

m:n ratio determined by 1H NMR to be approximately 1:1;

Found C, 70.0; H, 7.8; Br, 0.9; $[C_{32}H_{42}O_7]_n$ requires C, 71.4; H, 7.8; Br, 0%;

GPC assay in $CHCl_3$ revealed M_w 2.7×10^6 M_n 24×10^3 and M_w/M_n 110;

λ_{max} ($CHCl_3$)/nm 442; λ_{max} (film)/nm 452.



15C5-DMOS PPV copolymer, 13

A degassed solution of KO^tBu (0.16 g, 1.3 mmol) in dry THF (12 cm^3) was added slowly over 20 min to a degassed solution of a mixture of monomers, **10** (0.14 g, 0.3 mmol) and 2-methyloctylsilyl-1,4-bis(bromomethyl) benzene **11** (0.13 g, 0.3 mmol) in dry THF (13 cm^3) at room temperature. The reaction mixture was left stirring at ambient temperature under nitrogen for 8 h, after which it was poured into methanol (200 cm^3) with stirring. The resultant orange precipitate was collected, washed with methanol and dried *in vacuo*. The polymer was re-dissolved in minimum $CHCl_3$ and re-precipitated into methanol (200 cm^3). The solid was collected through filtration and dried *in vacuo* to afford the polymer as a right orange solid (0.13g, 76%).

ν_{max} (film)/ cm^{-1} 2923, 2856, 1459 (Ar), 1283, 1137 (C-O), 937 (trans-vinylene);

δ_H (400 MHz; $CDCl_3$) 7.67-6.95 (9H, m, br, H-conjugated unit), 4.22 (4H, s, br, $ArOCH_2$), 4.05 (4H, s, br, $ArOCH_2CH_2$), 3.79 (8H, s, br, OCH_2), 1.31-1.22 (12H, m, br, CH_2), 0.88 (5H, m, br, CH_2CH_3), 0.43-0.36 (6H, m, br, CH_3); m:n ratio determined by 1H NMR to be approximately 1:1;

Found C, 71.4; H, 8.3; Br, 1.9; $[C_{34}H_{48}O_5Si]_n$ requires C, 72.3; H, 8.6; Br, 0%;

GPC assay in $CHCl_3$ revealed M_w 286×10^3 M_n 37×10^3 and M_w/M_n 7.7;

λ_{mac} (CHCl₃)/nm 434; λ_{max} (film)/nm 442.

The PL efficiency and the EL efficiency of the copolymers 12 and 13 and the corresponding efficiencies of DMOS-PPV and 1 are shown in Table 1 below. In particular, the electroluminescence efficiency of 12 and 13 is high, whilst these copolymers still have good photoluminescence efficiencies.

Table 1: Summary of efficiency data for the polymers 12 and 13 in comparison with DMOS-PPV and DB-PPV 1.

Polymer	PL efficiency ^a (%)	EL internal quantum efficiency ^b (Cd/A)
15C5-DB PPV 12	38	0.35
15C5-DMOS PPV 13	48	0.3
DMOS-PPV	60	not available
DB-PPV 1	40	0.015

^ameasurements made on films

^bmeasurements made on ITO/polymer/Al devices, thickness 100-200 nm.

References

US 3,401,152, Wessling *et al.*

US 5,558,904, Hsieh *et al.*

US 5,189,136, Wudl, F.

J. H. Burroughes *et al.*, *Nature*, 1990, 365, 47.

H.G. Gilch *et al.*, *J. Poly. Sci. 1-A*, 1966, 4, 1337.

B. R. Hsieh *et al.*, *Adv. Mater.*, 1995, 7, 36.

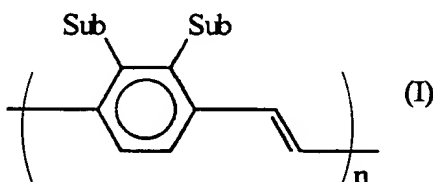
WO 95/32526, Staring & Demandt

H. Antoniadis *et al.*, *Poly. Adv. Tech.*, 1997, 8, 392

Claims:

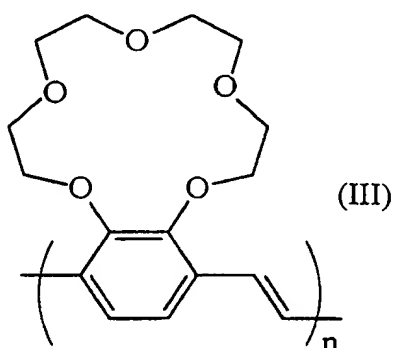
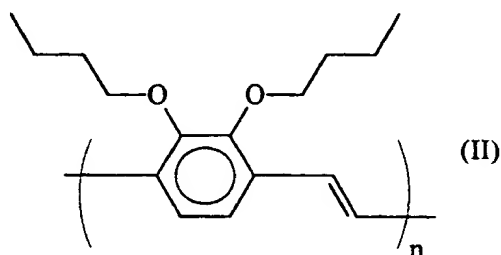
1. A conjugated poly(1,4-arylene vinylene) compound comprising an arylene unit having adjacent substituents, said substituents being oriented such as to affect the electronic structure of the compound sufficiently to cause a blue-shift in the photoluminescence and/or electroluminescence of the compound.
2. A compound according to claim 1, wherein the substituents are independently selected from:
 - (i) R-, RO-, RS-, and RR'N-
wherein R and R' are independently: a straight or branched chain alkyl group, alkenyl group, or alkynyl group having 1-10 carbon atoms; an aryl group; or an aromatic or non-aromatic heterocyclic group; and
 - (ii) a group in which the adjacent substituents together form a cyclic group, the cyclic group containing, in addition to the two carbon atoms of the arylene unit to which it is attached, 1-10 carbon atoms and 0 or 1-6 hetero atoms selected from O, S and N.
3. A compound according to claim 2, wherein the cyclic group contains 2-6 hetero atoms.
4. A compound according to any preceding claim, wherein one or both of the adjacent substituents are independently selected from a branched alkyl group and a branched alkoxy group.
5. A compound according to any preceding claim, wherein each of the carbon atoms at the adjacent substituted positions of the aryl unit is attached to its substituent via a hetero atom, selected from O, S or N.
6. A compound according to any preceding claim, wherein the substituents are solubilising substituents.

7. A compound according to any preceding claim, wherein one or both of the adjacent substituents are independently selected from butyloxy, ethylhexyloxy and 3',7'-dimethyloctyloxy groups.
8. A compound according to any preceding claim, wherein the arylene unit is a fluorene unit, a phenyl unit, a thienyl unit, a naphthalene unit, a pyridine unit, a quinoline unit, a quinoxaline unit, or a unit comprising a thienylene and a phenylene.
9. A compound according to any preceding claim, wherein the poly(arylene vinylene) is a copolymer comprising a fluorescent unit carrying a distyryl-2,3-substituted-benzene fragment.
10. A compound according to any preceding claim, which is a poly(phenylene vinylene) compound.
11. A compound according to claim 10, wherein the adjacent substituents are in the 2-position and the 3-position of the phenylene residue.
12. A compound according to claim 11, of formula (I):



wherein Sub is a substituent as defined in any of claims 1-7, the vinylene unit may be a trans vinylene unit or a cis vinylene unit, and n is the number of units of the formula in the polymer.

13. A compound according to claim 11, of formula (II) or formula (III):



wherein the vinylene unit may be a trans vinylene unit or a cis vinylene unit, and n is the number of units of the respective formula in the polymer.

14. A method for the production of a compound as defined in any preceding claim, which method comprises polymerising a bis(halomethyl) substituted aryl monomer in the presence of a base to form a poly(arylene vinylene), wherein the aryl monomer has adjacent substituents on the aryl residue.

15. A method according to claim 14, wherein the monomer is a bis(chloromethyl), bis(bromomethyl) or bis(iodomethyl) monomer.

16. A method according to claim 14 or claim 15, wherein the base is potassium tertiary butoxide.

17. A component or device comprising a compound as defined in any of claims 1-13.

18. A component or device according to claim 17, which is an electric, electronic, optical or optoelectronic component or device.
19. A component or device according to claim 17 or claim 18, which is a photoluminescent or electroluminescent component or device.
20. A light emitting diode comprising a component or device as defined in any of claims 17-19.
21. A method for producing a component or device as defined in any of claims 17-20, which method comprises coating a solution of a compound as defined in any of claims 1-13 onto a substrate to form a film.
22. A method according to claim 21, wherein the substrate is ITO.
23. A method according to claim 21 or claim 22, wherein the solution is a chloroform solution.
24. A method according to any of claims 21-23, wherein the solution is spin-coated onto the substrate.
25. Use of a light emitting diode as defined in claim 20, in an electric, electronic, optical or optoelectronic component or device.
26. Use of a poly(arylene vinylene) compound comprising an arylene unit having adjacent substituents, in an electric, electronic, optical or optoelectronic component or device for producing blue-shifted electroluminescence or photoluminescence in said device.
27. Use according to claim 26, wherein the adjacent substituents are as defined in any of claims 1-7.

28. Use according to claim 26 or claim 27, wherein the arylene unit is as defined in any of claims 8-13.
29. Use according to any of claims 26-28, wherein the electric, electronic, optical or optoelectronic component or device is a light emitting device, such as a light emitting diode.

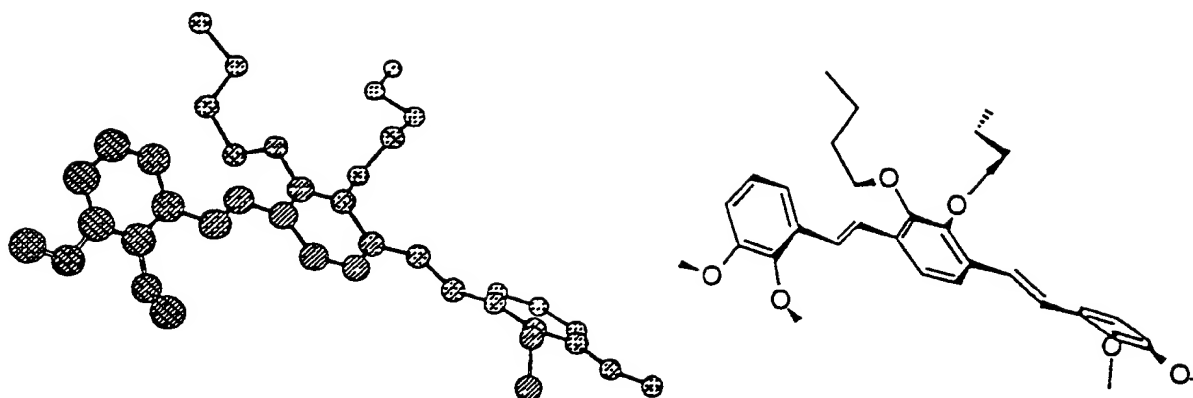


FIGURE 1

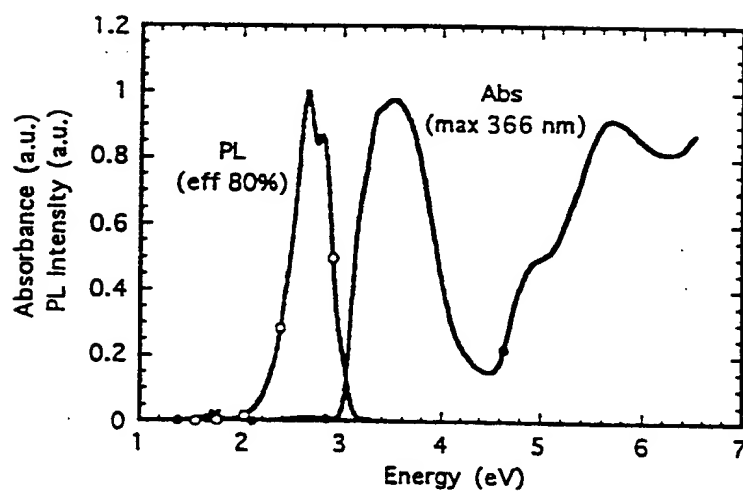


FIGURE 2

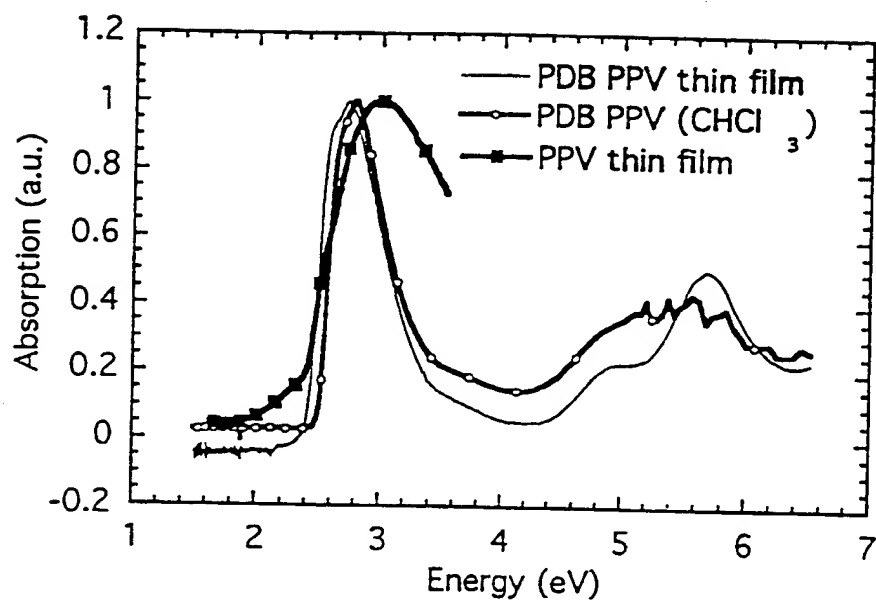


FIGURE 3

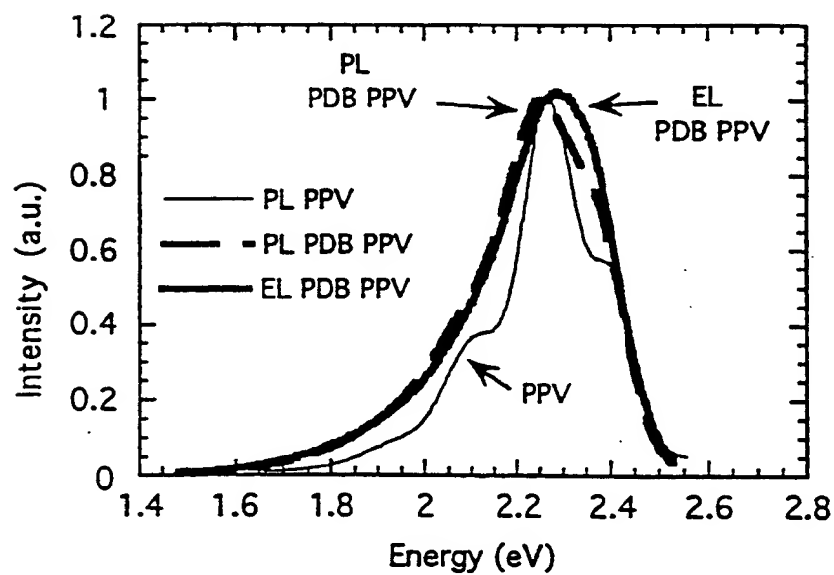


FIGURE 4

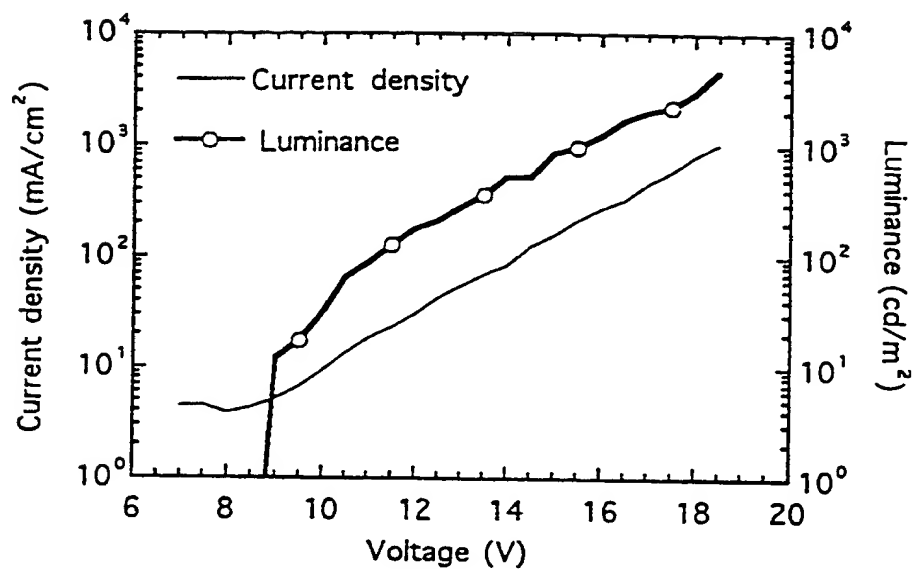


FIGURE 5

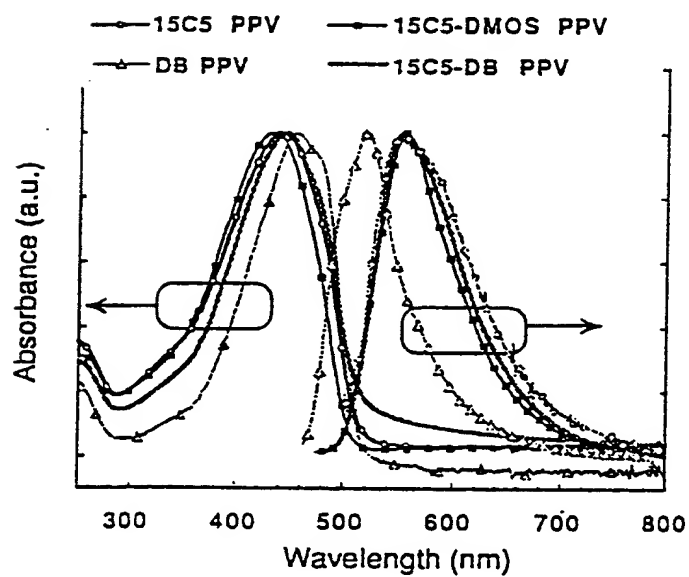


FIGURE 6

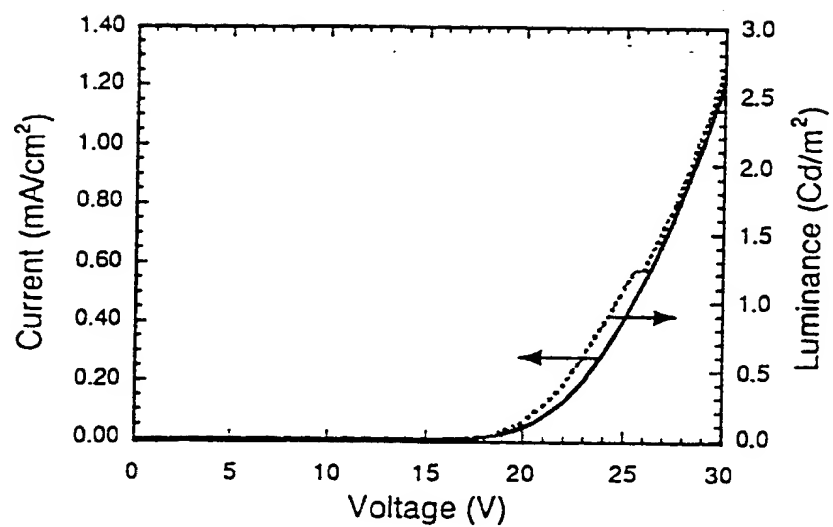


FIGURE 7

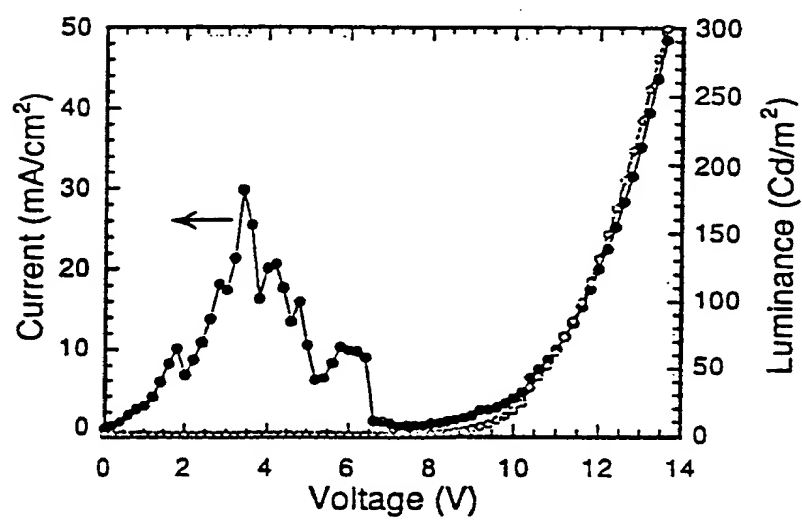


FIGURE 8

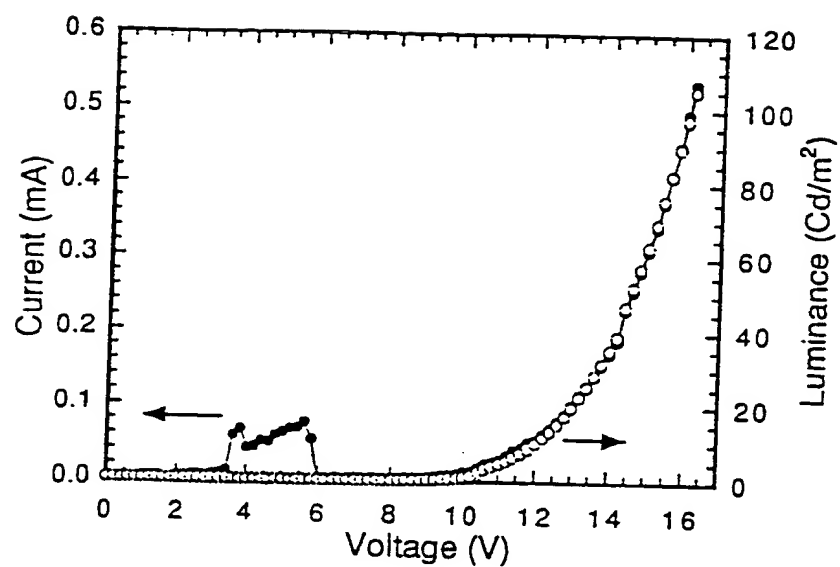


FIGURE 9

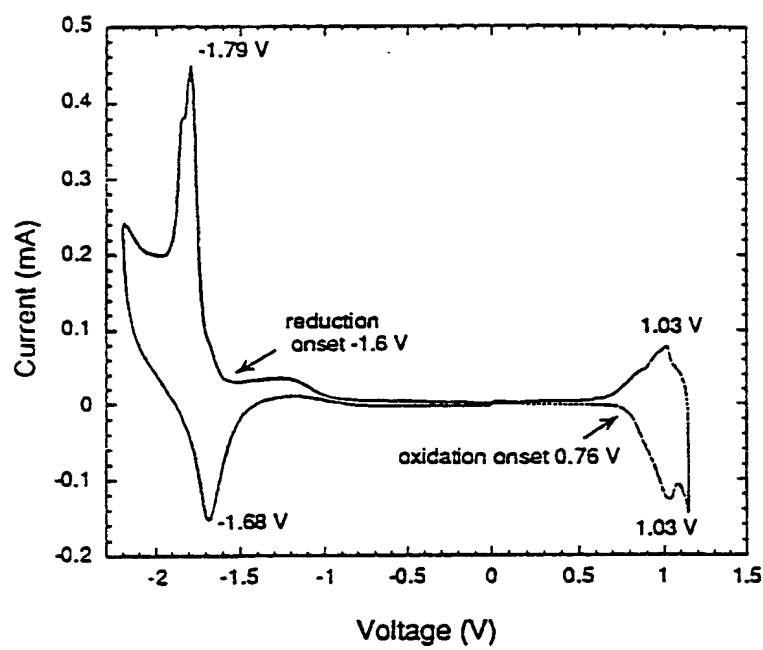


FIGURE 10

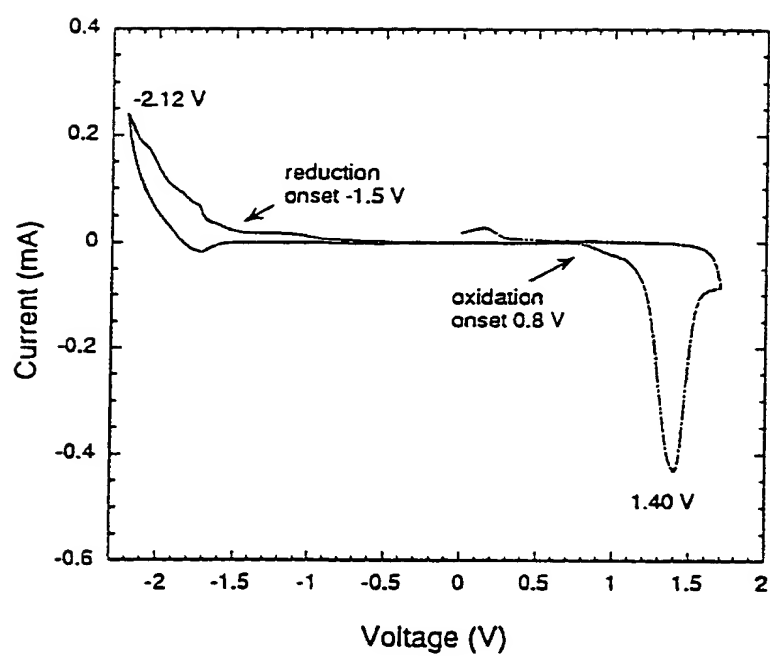


FIGURE 11

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09K11/06 H01B1/12 C08G61/10 H05B33/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K H01B C08G H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 745 658 A (STICHTING SCHEIKUNDIG ONDERZOE ;STICHTING TECH WETENSCHAPP (NL); U) 4 December 1996 see page 3, line 35 - line 45 ---	1,2,6,8, 10,17-29
X	US 5 558 904 A (HSIEH BING R ET AL) 24 September 1996 cited in the application see example 6 ---	1,2, 8-11, 14-29
X	WEI P K ET AL: "SURFACE MODIFICATION AND PATTERNING OF CONJUGATED POLYMERS WITH NEAR-FIELD OPTICAL MICROSCOPY" ADVANCED MATERIALS, vol. 8, no. 7, July 1996, pages 573-576, XP000598874 Scheme 2 --- -/--	1,2,8, 14-29

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

18 December 1998

Date of mailing of the international search report

12/01/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Shade, M

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>ANTONIADIS H ET AL: "LIGHT-EMITTING DIODES BASED ON POLY(2,3-DIPHENYL-1,4-PHENYLENE VINYLENE)" POLYMERS FOR ADVANCED TECHNOLOGIES, vol. 8, no. 7, July 1997, pages 392-398, XP000695518 cited in the application see the whole document</p>	1,2, 8-11, 14-29
X	<p>WAN W C ET AL: "HALOGEN PRECURSOR ROUTE TO POLY 2,3-DIPHENYL-P-PHENYLENE)VINYLENE (DP-PPV): SYNTHESIS, PHOTOLUMINESCENCE, ELECTROLUMINESCENCE, AND PHOTOCONDUCTIVITY" MACROMOLECULES, vol. 30, no. 21, 20 October 1997, pages 6567-6574, XP000720388 see the whole document</p>	1,2,8, 11,14-29
A	<p>GETTINGER ET AL: "A photoluminescence study of poly(phenylene vinylene) derivatives: The effect of intrinsic persistence length" JOURNAL OF CHEMICAL PHYSICS, vol. 101, no. 2, 15 July 1994, pages 1673-1678, XP002088538 see the whole document</p>	1-29
A	<p>WOO: "Optical spectra and excitations in phenylene vinylene oligomers" SYNTHETIC METALS, vol. 59, 1993, pages 13-28, XP002088539 see the whole document</p>	1-29
A	<p>US 5 514 878 A (HOLMES ANDREW B ET AL) 7 May 1996 see the whole document</p>	1-29

INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/GB 98/03154

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0745658	A	04-12-1996	NONE	
US 5558904	A	24-09-1996	NONE	
US 5514878	A	07-05-1996	AU 6729194 A EP 0704094 A WO 9429883 A	03-01-1995 03-04-1996 22-12-1994